

(10)日本国特許庁(JP)

(12)公開特許公報(A)

(11)特許出願公開番号

特開平6-290810

(43)公開日 平成6年(1994)10月18日

(51)InLCl₃
H 0 1 M 16/40
6/18

案別記号 戸内登録番号
B E

F I

技術表示箇所

審査請求 未請求 請求項の数3 FD (全5頁)

(21)出願番号 特願平5-90879

(22)出願日 平成5年(1993)3月30日

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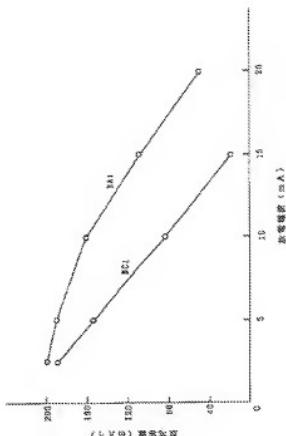
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(54)【発明の名称】 固体電解質電池

(57)【要約】

【構成】 L i P F₆ を溶質とする有機電解液に、前記 L i P F₆ を重合触媒として重合硬化可能なモノマーを添加混合して得たスラリーを、正極及び負極上に塗布し、これら両電極のスラリー塗布面を重ね合わせたのち加熱して、前記モノマーを重合硬化させるとともに、前記有機電解液中の有機溶媒を蒸発させてなる固体電解質が使用されてなるか、或いは、L i C l O₄、L i C F₃ S O₃、L i A l C l₄ 又はC a (A l C l)₄ を溶質とする有機電解液に、重合触媒及び当該重合触媒により重合硬化可能なモノマーを添加混合して得たスラリーを、正極及び負極上に塗布し、これら両電極のスラリー塗布面を重ね合わせたのち加熱して、前記モノマーを重合硬化させるとともに、前記有機電解液中の有機溶媒を蒸発させてなる固体電解質が使用されてなる。

【効果】 電極上でモノマーを重合硬化させてなるところの、電極との密着性に優れた固体電解質が使用されてるので、高率放電特性に優れるとともに、二次電池にあってはさらにはサイクル特性にも優れる。



【特許請求の範囲】

【請求項1】 LiPF_6 を溶質とする有機電解液に、前記 LiPF_6 を重合触媒として重合硬化可能なモノマーを添加混合して得たスラリーを、正極及び負極上に塗布し、これら両電極のスラリー塗布面を重ね合わせたのち加熱して、前記モノマーを重合硬化させるとともに、前記有機電解液中の有機溶媒を蒸発させてなる固体電解質が使用されていることを特徴とする固体電解質電池。

【請求項2】 LiClO_4 、 LiCF_3SO_3 、 LiAlCl_4 又は $\text{Ca}(\text{AlCl})_4$ を溶質とする有機電解液に、重合触媒及び当該重合触媒により重合硬化可能なモノマーを添加混合して得たスラリーを、正極及び負極上に塗布し、これら両電極のスラリー塗布面を重ね合わせたのち加熱して、前記モノマーを重合硬化させるとともに、前記有機電解液中の有機溶媒を蒸発させてなる固体電解質が使用されていることを特徴とする固体電解質電池。

【請求項3】 前記モノマーが 1, 3-ジオキサン、4-メチル-1, 3-ジオキサン、テトラヒドロフラン又は 2-メチルテトラヒドロフランである請求項1又は2記載の固体電解質電池。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明は固体電解質電池に係わり、詳しくは固体電解質と電極との間の界面抵抗が小さい固体電解質電池を得ることを目的とした固体電解質の改良に関する。

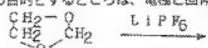
【0002】

【従来の技術及び発明が解決しようとする課題】 近年、ポリエチレンオキサイド (PEO)、ポリフロビレンオキサイド (PPO) などのイオン導電性ポリマーを電解質とする固体電解質電池が、漏れれか無くポジションフリーであることから、注目を集めている。

【0003】 従来の固体電解質電池は、各別に作製した電極を固体電解質を介して、積層し或いは巻き巻き状に巻き取ったのち電池缶内に収納し、封口することにより作製されていた。

【0004】 しかしながら、このようにして作製された固体電解質電池では、電極と固体電解質とは単に圧接されているに過ぎず密着性が良くないため、剥離し易く、またこれら両者間の界面抵抗が大きい。このため、従来の固体電解質電池には、高率放電特性や、二次電池にあってはさらにはサイクル特性が良くないという問題があつた。

【0005】 本発明は、この問題を解決すべくなされたものであつて、その目的とするところは、電極と固体



【0006】 本発明電池における有機電解液としては、

電解質との密着性が良い、高率放電特性やサイクル特性(二次電池の場合)に優れた固体電解質電池を提供するにある。

【0006】

【課題を解決するための手段】 上記目的を達成するための請求項1記載の発明に係る固体電解質電池(以下、「第1電池」と称する。)は、 LiPF_6 を溶質とする有機電解液に、前記 LiPF_6 を重合触媒として重合硬化可能なモノマーを添加混合して得たスラリーを、正極及び負極上に塗布し、これら両電極のスラリー塗布面を重ね合わせたのち加熱して、前記モノマーを重合硬化させるとともに、前記有機電解液中の有機溶媒を蒸発させてなる固体電解質が使用されてなる。

【0007】 また、請求項2記載の発明に係る固体電解質電池(以下、「第2電池」と称する。)は、 LiClO_4 、 LiCF_3SO_3 、 LiAlCl_4 又は $\text{Ca}(\text{AlCl})_4$ を溶質とする有機電解液に、重合触媒及び当該重合触媒により重合硬化可能なモノマーを添加混合して得たスラリーを、正極及び負極上に塗布し、これら両電極のスラリー塗布面を重ね合わせたのち加熱して、前記モノマーを重合硬化させるとともに、前記有機電解液中の有機溶媒を蒸発させてなる固体電解質が使用されてなる。なお、以下においては第1電池と第2電池と総称する場合、本発明電池と称することにする。

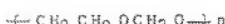
【0008】 本発明電池は、重合触媒の存在下、重合可能なモノマーを重合硬化させてなる固体電解質が使用される。モノマーの具体例としては、1, 3-ジオキサン、4-メチル-1, 3-ジオキサン、テトラヒドロフラン、2-メチルテトラヒドロフランが挙げられる。

【0009】 第1電池においては、有機電解液の溶質たる LiPF_6 がモノマーの重合触媒として機能するので別途重合触媒を加える必要は無いが、第2電池においては、有機電解液の溶質たる LiClO_4 、 LiCF_3SO_3 、 LiAlCl_4 及び $\text{Ca}(\text{AlCl})_4$ が重合触媒として機能しないので別途 AlCl_3 などの重合触媒を加える必要がある。なお、有機電解液の溶質として LiPF_6 を使用する場合であっても、重合反応を促進するため、 AlCl_3 等の他の重合触媒を別途添加するようにしてよい。

【0010】 上記モノマーの重合反応を、1, 3-ジオキサンを使用する場合を例に挙げて示すと、次の化1に示す通りであり、この場合の重合反応は環状エーテルの開環重合である。

【0011】

【化1】



エチレンカーボネート、ビニレンカーボネート、プロピ

レンカーボネットなどの有機溶媒や、これらとジメチルカーボネット、ジエチルカーボネット、1, 2-ジメチキシエタン、1, 2-ジエトキシエタン、エトキシメチキシエタンなどの低沸点溶媒との混合溶媒に、溶質としてのLiPF₆、LiClO₄、LiCF₃SO₃、LiAlCl₄又はCa(AlCl)₄を浴かした溶液が例示される。

【0013】上述したように、本発明は、電極上で重合反応させて得た固体電解質を使用した点に特徴を有する。それゆえ、正極材料、負極材料などの電池を構成する他の部材については特に制限されず、固体電解質電池用として従来使用され、或いは提案されている種々の材料を制限無く使用することが可能である。

【0014】例えば、正極材料(活性物質)としては、LiCO₂、LiNiO₂、LiMnO₂、LiFeO₂が適なものとして挙げられる。

【0015】また、負極材料としては、黒鉛、コーカス等の炭素材料その他、金属酸化物などが例示される。炭素材料の中では、放電容量の大きな電池を得る上で、格子面(002)面におけるd値(d₀₀₂)が3.37 Å未満でc軸方向の結晶子の大きさ(Lc)が2.00 Å以上の場合に高い放電特性が特に好ましい。

【0016】

【作用】本発明電池においては、電極上でモノマーを重合硬化させて形成された固体電解質が使用されているので、固体電解質と商電極との密着性が良い。このため、充放電サイクルを重ねても剥離しにくく、また界面抵抗が小さいで高率放電特性に優れる。

【0017】

【実施例】以下、本発明を実施例に基づいてさらに詳細に説明するが、本発明は下記実施例により何ら限界されるものではなく、その要旨を変更しない範囲において適宜変更して実施することが可能なものである。

【0018】【実施例】扁平角型の固体電解質二次電池(本発明電池)を作製した。

【0019】【正極】正極活性物質としてのLiCoO₂と、導電剤としての人造黒鉛と、ポリテトラフルオロエチレンとを、重量比率90:5:5で混合して正極合剤を得た。次いで、この正極合剤を成形圧2トン/cm²で加圧成形した後、250°Cで加熱処理して、正極を作製した。なお、正極集電体として、ステンレス鋼板(SUS304)を使用した。

【0020】【負極】負極材料としての天然黒鉛と、接着剤としてのポリテトラフルオロエチレンとを、重量比率95:5で混合して負極合剤を得た。次いで、この負極合剤を成形圧2トン/cm²で加圧成形した後、250°Cで加熱処理して、負極を作製した。なお、負極集電体として、ステンレス鋼板(SUS304)を使用した。

【0021】【固体電解質】アセトニトリルにLiPF₆

6(純度99.9%)を1Mの割合で浴かして有機電解液を調製した。次いで、この有機電解液500ccに、1, 3-ジオキソラン(モノマー)50ccを添加混合してスラリーを作製した。このスラリーを正極及び負極の片面にドクターブレード法により厚さ10μmに塗布した後、両電極の塗布面を重ね合わせ、60°Cで2時間加熱して、アセトニトリルを蒸発させるとともに、スラリーを硬化させて、固体電解質を両電極と一緒に形成した。

【0022】【電池の作製】これらの一體化された正負両極及び固体電解質を電池缶内に収納して扁平角型の本発明電池B A 1(電池寸法: 縦横10×5cm、厚み0.5mm)を作製した。

【0023】図1は作製した本発明電池B A 1を模式的に示す断面図であり、同図に示す本発明電池B A 1は、正極1、負極2、これら両電極1、2を互いに離隔するセパレータを兼ねる固体電解質3、正極缶4、負極缶5、正極集電体6、負極集電体7及びボリフロビレン製の絶縁パッキング8などからなる。

【0024】正極1及び負極2は、固体電解質3を介して対向して正負両極缶4、5が形成する電池ケース内に収納されており、正極1は正極集電体6を介して正極缶4に、また負極2は負極集電体7を介して負極缶5に接続され、電池内部で生じた化学エネルギーを正極缶4及び負極缶5の両端子から電気エネルギーとして外部へ取り出し得るようになっている。

【0025】【比較例】ボリオキシメチレン樹脂のメチルエチルケトン(MEK)溶液(樹脂固形分: 10重量%)250ccに、アセトニトリル250ccにLiPF₆を0.5Mの割合で浴かして有機電解液を混合して得たスラリーを、ガラス板上にドクターブレード法により厚さ10μmに塗布し、60°Cで2時間乾燥してMEKとアセトニトリルを蒸発させて、薄膜状の固体電解質をガラス板上に生成させた。次いで、この固体電解質を先の実施例で使用したものと同様の正極及び負極の間に挟み込んだ状態で電池缶内に収納して、比較電池B C 1を作製した。

【0026】【両電池の放電容量】先ず、室温(25°C)下、2.0mAで充電終止電圧4.2Vまで充電した後、2.0mAで放電終止電圧2.5Vまで放電した。次いで、再び2.0mAで充電終止電圧4.2Vまで充電した後、種々の電流で放電して、両電池の放電容量を調べた結果を図2に示す。

【0027】図2は、両電池の種々の放電電流における放電容量を、絶縁に放電容量(mAh)を、横軸に放電電流(mA)をとって示したグラフであり、同図より、固体電解質が電極上に一体形成された本発明電池B A 1は、固体電解質が電極上に単に堆積されているに過ぎない比較電池B C 1に比し、両者間の界面抵抗が小さいため高率放電特性に優れていることが分かる。

【0028】 [両電池のサイクル特性] 室温(25°C)下、2.5mAで充電終止電圧4.2Vまで充電した後、2.5mAで放電終止電圧2.0Vまで放電する工程を1サイクルとするサイクル試験を行い、両電池のサイクル特性を調べた。結果を図3に示す。

【0029】図3は、両電池のサイクル特性を、縦軸に放電容量(mAh)を、横軸にサイクル数(回)をとつて示したグラフであり、同図より、本発明電池B A 1は、比較電池B C 1に比し、電極と固体電解質との密着性が良く剥離にくいため高率放電特性に優れていることが分かる。

【0030】図3の実施例では、本発明を扁平角型の固体電解質二次電池に適用する場合を例に挙げて説明したが、電池の形状は特に限定されない。

【0031】また、実施例では、リチウムイオンを電荷担体とする固体電解質リチウム二次電池を例に挙げて説明したが、本発明は、ナトリウムイオン等の他のアルカリ金属イオン又はカルシウムイオン等のアルカリ土類金属イオンを電荷担体とする固体電解質電池にも適用し得るものであり、また一次電池であるか、二次電池であるかについても問われない。

【0032】さらに、実施例では、LiPF₆を溶質とする有機電解液を使用したが、LiClO₄等を溶質と

する有機電解液を使用し、別途重合触媒を加えてモノマーを重合硬化させるようにしても本発明電池B A 1と同様の高率放電特性及びサイクル特性に優れた固体電解質二次電池を得ることが可能である。

【0033】

【発明の効果】 本発明電池は、電極上でモノマーを重合硬化させてなるところの、電極との密着性に優れた固体電解質が使用されているので、高率放電特性に優れるとともに、二次電池にあってはさらにサイクル特性にも優れるなど、本発明は優れた特有の効果を奏す。

【図面の簡単な説明】

【図1】 扁平角型の固体電解質電池(本発明電池)の断面図である。

【図2】 実施例及び比較例で作製した各電池を種々の電流で放電したときの放電容量を示すグラフである。

【図3】 実施例及び比較例で作製した各電池のサイクル特性を示すグラフである。

【符号の説明】

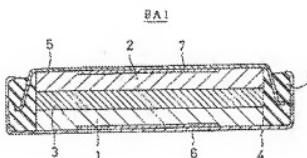
B A 1 固体電解質電池(本発明電池)

1 正極

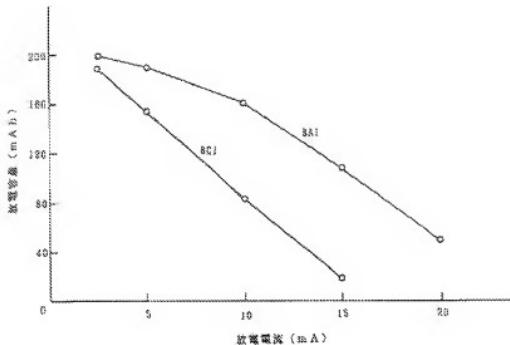
2 負極

3 セパレータ

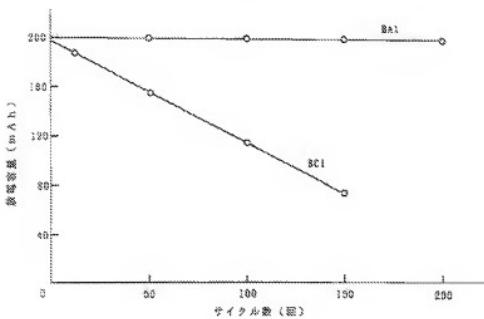
【図1】



【図2】



【図3】



フロントページの続き

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PATENT ABSTRACTS OF JAPAN

(11) Publication number : 06-290810

(43) Date of publication of application : 18.10.1994

(51) Int. Cl.

HO1M 10/40

HO1M 6/18

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(22) Date of filing : 30.03.1993 (72) Inventor : FUJIMOTO MASAHISA

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(54) SOLID ELECTROLYTE BATTERY

(57) Abstract:

PURPOSE: To provide a solid electrolyte battery, which is excellent in a high rate discharging characteristic and a recycling characteristic (in the case of a secondary battery), by providing a solid electrolyte having good adhesiveness to an electrode formed by polymerizing and curing a monomer on the electrode.

CONSTITUTION: A solid electrolyte battery BAI consists of a positive electrode 1, a negative electrode 2, a solid electrolyte 3, which simultaneously serves as a separator for separating both of the positive electrode 1 and the negative electrode 2 from each other, a positive electrode can 4, a negative electrode can 5, a positive electrode collecting body 6, a negative electrode collecting body 7, an insulating packing 8, and the like. The solid electrolyte is formed in a following way. Slurry obtained by adding and mixing a monomer, which can be polymerized and cured by employing LiPF₆ as a polymerizing catalyst, with an organic electrolyte using LiPF₆ as a solute is applied on the positive electrode and the negative electrode. Both of the electrodes applied with the slurry are put together and heated, so that the monomer is polymerized and cured, while an organic solvent in the organic electrolyte is evaporated. LiClO₄, LiCF₃SO₃, LiAlCl₄, or ca(AlCl)₄ is

available in stead of LiPF6.

LEGAL STATUS

[Date of request for examination] 08.10.1999

[Date of sending the examiner's
decision of rejection]

[Kind of final disposal of
application other than the
examiner's decision of rejection or
application converted registration]

[Date of final disposal for
application]

[Patent number] 3203093

[Date of registration] 22.06.2001

[Number of appeal against
examiner's decision of rejection]

[Date of requesting appeal against
examiner's decision of rejection]

[Date of extinction of right]

CLAIMS

[Claim(s)]

[Claim 1] LiPF6 To the organic electrolytic solution made into a solute, it is said LiPF6. Solid electrolyte cell characterized by to use the solid electrolyte which makes the organic solvent in said organic electrolytic solution come to evaporate while the slurry which carried out addition mixing and obtained the monomer in which polymerization hardening is possible is applied on a positive electrode and a negative electrode, it considers as a polymerization catalyst, it heats after piling up the slurry spreading side of these two electrodes, and carrying out polymerization hardening of said monomer.

[Claim 2] LiClO4, LiCF3 SO3, and LiAlCl4 Or calcium4 (AlCl) To the organic electrolytic solution made into a solute While the slurry which carried out addition mixing of the monomer in which polymerization hardening is possible according to the polymerization catalyst and the polymerization catalyst concerned, and was obtained is applied on a

positive electrode and a negative electrode, it heats after piling up the slurry spreading side of these two electrodes, and carrying out polymerization hardening of said monomer. The solid electrolyte cell characterized by using the solid electrolyte which makes the organic solvent in said organic electrolytic solution come to evaporate.

[Claim 3] The solid electrolyte cell according to claim 1 or 2 said whose monomer is 1, 3-dioxolane, the 4-methyl -1, 3-dioxolane, a tetrahydrofuran, or 2-methyl tetrahydrofuran.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to amelioration of the solid electrolyte aiming at obtaining a solid electrolyte cell with the interfacial resistance it being detailed and small between a solid electrolyte and an electrode with respect to a solid electrolyte cell.

[0002]

[Description of the Prior Art] In recent years, by there being no liquid spill, since the solid electrolyte cell which uses ion conductive polymers, such as polyethylene oxide (PEO) and polypropylene oxide (PPO), as an electrolyte is a position free-lancer, it attracts attention.

[0003] The conventional solid electrolyte cell was produced by containing and obturating in a cell can, after carrying out the laminating of the electrode produced to each ** through the solid electrolyte or rolling round to a curled form.

[0004] however, in the solid electrolyte cell produced by doing in this way, the pressure welding of an electrode and the solid electrolyte is only carried out -- **** -- it does not pass, but since adhesion is not good, it is easy to exfoliate, and the interfacial resistance between these both is large. For this reason, if it was in the high-rate-discharge property and the rechargeable battery, there was a problem that a cycle property was not still better in the conventional solid electrolyte cell.

[0005] The place which this invention is made so that it may solve this problem, and is made into that purpose has the adhesion of an electrode and a solid electrolyte in offering the solid electrolyte cell excellent in a good high-rate-discharge property and a good cycle property (in the

case of a rechargeable battery).

[0006]

[Means for Solving the Problem] The solid electrolyte cell ("the 1st cell" is called hereafter.) concerning invention according to claim 1 for attaining the above-mentioned purpose LiPF6 To the organic electrolytic solution made into a solute, it is said LiPF6. It heats, after considering as a polymerization catalyst, applying the slurry which carried out addition mixing and obtained the monomer in which polymerization hardening is possible on a positive electrode and a negative electrode and piling up the slurry spreading side of these two electrodes. While carrying out polymerization hardening of said monomer, it comes to use the solid electrolyte which makes the organic solvent in said organic electrolytic solution come to evaporate.

[0007] Moreover, the solid electrolyte cell ("the 2nd cell" is called hereafter.) concerning invention according to claim 2 LiClO4, LiCF3 SO3, and LiAlCl4 Or calcium4 (AlCl) To the organic electrolytic solution made into a solute While the slurry which carried out addition mixing of the monomer in which polymerization hardening is possible according to the polymerization catalyst and the polymerization catalyst concerned, and was obtained is applied on a positive electrode and a negative electrode, it heats after piling up the slurry spreading side of these two electrodes, and carrying out polymerization hardening of said monomer It comes to use the solid electrolyte which makes the organic solvent in said organic electrolytic solution come to evaporate. In addition, when naming it the 1st cell and the 2nd cell generically below, this invention cell will be called.

[0008] The solid electrolyte with which this invention cell comes to carry out polymerization hardening of the monomer in which a polymerization is possible under existence of a polymerization catalyst is used. As an example of a monomer, 1, 3-dioxolane, the 4-methyl -1, 3-dioxolane, a tetrahydrofuran, and 2-methyl tetrahydrofuran are mentioned.

[0009] the 1st cell -- setting -- the organic electrolytic solution -- a solute -- LiPF6 although there is no need of adding a polymerization catalyst separately since it functions as a polymerization catalyst of a monomer -- the 2nd cell -- setting -- the organic electrolytic solution -- a solute -- LiClO4, LiCF3 SO3, and LiAlCl4 And calcium (AlCl)4 since it does not function as a polymerization catalyst -- separately -- AlCl3 etc. -- it is necessary to add a polymerization catalyst in addition -- as the solute of the organic electrolytic solution -- LiPF6 even if it is the case where it is used, in order to promote a polymerization reaction -- AlCl4 etc. -- you may make it add other polymerization

catalysts separately

[0010] When the case where 1 and 3-dioxolane is used for the polymerization reaction of the above-mentioned monomer is mentioned as an example and shown, it is as being shown in next ** 1, and the polymerization reaction in this case is the ring opening polymerization of cyclic ether.

[0011]

[Formula 1]



[0012] As the organic electrolytic solution in this invention cell, they are LiPF₆ as a solute, LiClO₄, LiCF₃SO₃, and LiAlCl₄ to the mixed solvent of organic solvents, such as ethylene carbonate, vinylene carbonate, and propylene carbonate, these, and low-boiling point solvents, such as dimethyl carbonate, diethyl carbonate, 1, 2-dimethoxyethane, 1, 2-diethoxy ethane, and ethoxy methoxyethane. Or calcium⁴ (AlCl) The melted solution is illustrated.

[0013] As mentioned above, this invention has the description at the point which used the solid electrolyte which was made to carry out a polymerization reaction and was obtained on the electrode. So, it is possible to use it without a limit of the various ingredients which are not restricted especially about other members which constitute cells, such as a positive-electrode ingredient and a negative-electrode ingredient, are conventionally used as an object for solid electrolyte cells, or are proposed.

[0014] For example, as a positive-electrode ingredient (active material), they are LiCoO₂, LiNiO₂, LiMnO₂, and LiFeO₂. It is mentioned as a suitable thing.

[0015] Moreover, as a negative-electrode ingredient, a metallic oxide besides carbon materials, such as a graphite and corks, etc. is illustrated. When obtaining a cell with a big discharge capacity in a carbon material, d value (d002) in a lattice plane (002) side has [especially a crystalline high graphite 200A or more] the magnitude (Lc) of the microcrystal of the direction of a c-axis desirable at less than 3.37A.

[0016]

[Function] In this invention cell, since the solid electrolyte which was made to carry out polymerization hardening of the monomer, and was formed on the electrode is used, the adhesion of a solid electrolyte and two electrodes is good. For this reason, even if it piles up a charge-

and-discharge cycle, it is hard to exfoliate, and since interfacial resistance is small, it excels in a high-rate-discharge property.

[0017]

[Example] It is possible to change this invention suitably in the range which is not limited at all by the following example and does not change the summary, and to carry out hereafter, although this invention is further explained to a detail based on an example.

[0018] [Example] The solid electrolyte rechargeable battery (this invention cell) of a flat square shape was produced.

[0019] a [positive electrode] -- LiCoO₂ as positive active material the artificial graphite as an electric conduction agent, and polytetrafluoroethylene -- the weight ratio 90:5:5 -- mixing -- a positive electrode -- the mixture was obtained. subsequently, this positive electrode -- a mixture -- moulding pressure 2 t/cm² After carrying out pressing, it heat-treated by 250-degreeC and the positive electrode was produced. In addition, the stainless steel plate (SUS304) was used as a positive-electrode charge collector.

[0020] a [negative electrode] -- the natural graphite as a negative-electrode ingredient, and the polytetrafluoroethylene as a binder -- the weight ratio 95:5 -- mixing -- a negative electrode -- the mixture was obtained. subsequently, this negative electrode -- a mixture -- moulding pressure 2 t/cm² After carrying out pressing, it heat-treated by 250-degreeC and the negative electrode was produced. In addition, the stainless steel plate (SUS304) was used as a negative-electrode charge collector.

[0021] [Solid electrolyte] LiPP6 (99.9% of purity) was melted at a rate of 1M to the acetonitrile, and the organic electrolytic solution was prepared. Subsequently, to 500 cc of this organic electrolytic solution, addition mixing of the 1 and 3-dioxolane (monomer) 50cc was carried out, and the slurry was produced. After applying this slurry to 10 micrometers in thickness with a doctor blade method at one side of a positive electrode and a negative electrode, while heating the spreading side of two electrodes by superposition and 60-degreeC for 2 hours and evaporating the acetonitrile, the slurry was stiffened and the solid electrolyte was formed in one with two electrodes.

[0022] [Production of a cell] These positive/negative two poles and solid electrolytes that were unified were contained in the cell can, and this invention cell BA 1 (cell dimension: every direction of 10x5cm, thickness of 0.5mm) of a flat square shape was produced.

[0023] Drawing 1 is the sectional view showing the produced this invention cell BA 1 typically, and this invention cell BA 1 shown in

this drawing consists of the solid electrolyte 3 which serves as the separator which estranges mutually a positive electrode 1, a negative electrode 2, and these two electrodes 1 and 2, the positive-electrode can 4, the negative-electrode can 5, the positive-electrode charge collector 6, a negative-electrode charge collector 7, insulating packing 8 made from polypropylene, etc.

[0024] The chemical energy which it is contained in the cell case which a positive electrode 1 and a negative electrode 2 counter through a solid electrolyte 3, and the positive/negative two-poles cans 4 and 5 form, and the negative electrode 2 was connected to the positive-electrode can 4 for the positive electrode 1 through [again] the negative-electrode charge collector 7 at the negative-electrode can 5 through the positive-electrode charge collector 6, and was produced inside the cell can be taken out now to the exterior as electrical energy from the both-ends child of the positive-electrode can 4 and the negative-electrode can 5.

[0025] (Example of a comparison) In 250 cc (resin solid content: 10 % of the weight) of methyl-ethyl-ketone (MEK) solutions of polyoxymethylene resin, it is LiPF6 to acetonitrile 250cc. The slurry which mixed and obtained the organic electrolytic solution melted at a rate of 0.5M was applied to 10 micrometers in thickness with the doctor blade method on the glass plate, was dried by 60-degreeC for 2 hours, MEK and an acetonitrile were evaporated, and the thin film-like solid electrolyte was made to generate on a glass plate. Subsequently, where this solid electrolyte is put between the same positive electrode as what was used in the previous example, and a negative electrode, it contained in the cell can, and the comparison cell BC 1 was produced.

[0026] [Discharge capacity of both cells] First, the bottom of a room temperature (25-degreeC), and after charging to charge termination electrical-potential-difference 4.2V by 20mA, it discharged to discharge-final-voltage 2.5V by 20mA. Subsequently, after charging to charge termination electrical-potential-difference 4.2V by 20mA again, it discharged with various currents and the discharge capacity of both cells was investigated. A result is shown in drawing 2.

[0027] Drawing 2 is the graph which took discharge capacity (mAh) along the axis of ordinate, took the discharge current (mA) along the axis of abscissa, and showed the discharge capacity in the various discharge currents of both cells, and it turns out that this invention cell BA 1 by which the solid electrolyte was really formed on the electrode from this drawing is compared with the comparison cell BC 1 by which the pressure welding of the solid electrolyte is only carried out to the

electrode, and it excels in the high-rate-discharge property since the interfacial resistance between both is small.

[0028] [Cycle property of both cells] The bottom of a room temperature (25-degreeC), and after charging to charge termination electrical-potential-difference 4.2V by 25mA, the cycle trial which makes 1 cycle the process which discharges to discharge-final-voltage 2.0V by 25mA was performed, and the cycle property of both cells was investigated. A result is shown in drawing 3.

[0029] It is the graph which drawing 3 took discharge capacity (mAh) along the axis of ordinate, took the number of cycles (time) along the axis of abscissa, and showed the cycle property of both cells, and since this invention cell BA 1 is compared with the comparison cell BC 1 and the adhesion of an electrode and a solid electrolyte cannot exfoliate easily well from this drawing, it turns out that it excels in the high-rate-discharge property.

[0030] Although the case where this invention was applied to the solid electrolyte rechargeable battery of a flat square shape was mentioned as the example and the above-stated example explained it, especially the configuration of a cell is not limited.

[0031] Moreover, although the solid electrolyte lithium secondary battery which makes a lithium ion a charge carrier was mentioned as the example and the example explained it, this invention can be applied also to the solid electrolyte cell which makes a charge carrier alkaline-earth-metal ion, such as other alkali-metal ion, such as sodium ion, or calcium ion, and is not asked about whether it is a primary cell or it is a rechargeable battery, either.

[0032] furthermore -- an example -- LiPF₆ although the organic electrolytic solution made into a solute was used -- LiClO₄ etc. -- even if it uses the organic electrolytic solution made into a solute, it adds a polymerization catalyst separately and it is made to carry out polymerization hardening of the monomer, it is possible to obtain the solid electrolyte rechargeable battery excellent in the same high-rate-discharge property as this invention cell BA 1 and the cycle property.

[0033]

[Effect of the Invention] This invention does the outstanding characteristic effectiveness so -- if it is in a rechargeable battery, this invention cell is further excellent also in a cycle property, while it is excellent in a high-rate-discharge property, since the solid electrolyte excellent in adhesion with the electrode which comes to carry out polymerization hardening of the monomer on an electrode is used.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the sectional view of the solid electrolyte cell (this invention cell) of a flat square shape.

[Drawing 2] It is the graph which shows the discharge capacity when discharging each cell produced in the example and the example of a comparison with various currents.

[Drawing 3] It is the graph which shows the cycle property of each cell produced in the example and the example of a comparison.

[Description of Notations]

BA1 Solid electrolyte cell (this invention cell)

1 Positive Electrode

2 Negative Electrode

3 Separator
